I. On the Reaction of Both the Ions and Molecules of Acids, Bases and Salts.

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VI. The Equilibrium Between Mucic Acid and Its Lactones.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

WILLIAM A. TAYLOR.

BALTIMORE,

May, 1914.

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I. On the Reaction of Both the Ions and Molecules of Acids, Bases and Salts.

On the Reaction of Sodium Ethylate and Methyl Iodide In Absolute Ethyl Alcohol at O°.

Until comparatively recently chemical transformations were thought by most chemists to be purely ionic. This was a natural consequence of the development of the theory of electrolytic dissociation by Arrhenius, especially since the earlier work on the hydrolysis of sugars, esters and amides by acids and the saponifications of esters by bases showed that these reactions are, in dilute solutions, nearly proportional to the concentration of the ions of the catalyzers. The natural conclusion was drawn that the reactions are brought about simply by the ions present. Notable among the opponents of this theory were Kahlenberg, Michael and Armstrong. Kahlenberg's work[1] was especially important as, besides other cases, he studied a number of very rapid reactions in nonaqueous solvents in which no appreciable ionization could be detected. As a result of this he came to the conclusion that the purely ionic theory of all chemical reactions was not established beyond question.

The work of Brunel[2] and Acree in 1905–6, of Johnson[3] and Acree in 1907 and the later work of Shadinger, Nirdlinger, Rogers, Chandler, Marshall, Robertson, Harrison, Shrader and Brown brought out an entirely new principle in catalysis,—namely, that acceleration may take place through the action of the nonionized acids, bases and salts, as well as through

[1] Jour. Phys. Chem., 5, 339; 6, 1, and other articles.
[2] Amer. Chem. Jour., 43, 505.
[3] Ibid., 38, 259, 260.

the ions. In the case of the rearrangement of acetylchloraminobenzene, Johnson and Acree found that the reaction took place almost entirely through the nonionized salt according to the equation:—

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \leftrightarrows CH_3CONHCl_2C_6H_5 \rightarrow$$
$$CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}$$

This theory has now been adopted generally to explain the "deviations" from the ionic reaction, and in the case of the hydrolysis of cane sugar by hydrochloric acid Worley[4] has shown that the molecular reaction is so great that its velocity is about twelve times that of the ionic reaction, as is shown in the following table:—

Molecular Proportions H_2O:HCl	Molecular Hydrolytic Activity of Acid	Degree of "Ionization" μ_v/μ_∞
30	385	0.725
40	323	0.778
50	290	0.813
60	269	0.837
80	243	0.859
100	229	0.871
2000	201	0.901
Dilutions (Mols. H_2O)	K_i	K_m
30:60	100	1136
30:80	94	1154
30:100	91	1160
30:200	98	1143
40:80	104	1092
40:100	99	1110
40:200	103	1095

[4] Phil. Mag. for Mch., 1914.

50:80	99	1121
50:100	92	1145
50:200	101	1112
60:100	77	1154
60:200	96	1159
80:100	79	1245
80:200	102	1102
100:200	109	1042
Mean	96	1138

The work which was taken up in this laboratory to prove this theory quantitatively was chiefly the reactions of ethylates and phenolates with alkyl halides. These substances were chosen because here we have a nonelectrolyte reacting with a univalent electrolyte whose ionization varies over a wide range. Then, too, in these cases, we are not hindered by troublesome side reactions, and the transformations are also easily controlled and easily and accurately determined.

In the present piece of work we took up the study of the reaction of sodium ethylate with methyl iodide at 0°, repeating the work of Miss B. M. Brown, to see if the same constants could be obtained by two independent workers.

If both the ethylate ions and the nonionized ethylate react we should have two reactions going on side by side, the velocity of one of which is proportional to the concentration of the ionized ethylate and the other proportional to the concentration of the nonionized ethylate, according to the equations:—

$$\text{Ionic: } C_2H_5I + C_2\bar{H}_5O + \overset{+}{Me} \rightarrow (C_2H_5)_2O + \overset{+}{Me} + \bar{I}$$

$$\text{Molecular: } C_2H_5I + C_2H_5OMe \rightarrow (C_2H_5)_2O + \overset{+}{Me} + \bar{I}$$

If we represent by K_i the velocity constant for the ionic reaction, by K_m the velocity constant for the molecular reac-

tion, and by K_N the total velocity constant, in solutions having unit concentrations, by x the change in concentration of the ethylate in time t, by C_{ethylate} the initial concentration of the ethylate in gram mols per liter, by $C_{\text{alkyl halide}}$ the initial concentration of alkyl halide in gram mols per liter, we have the equation:—

$$dx/dt = K_i a(C_{\text{ethylate}} - x)\,(C_{\text{alkyl halide}} - x) + K_m(1 - a)\,(C_{\text{ethylate}} - x)\,(C_{\text{alkyl halide}} - x)$$

If we represent C_{ethylate} by A and $C_{\text{alkyl halide}}$ by B, we obtain on integrating the above equation

$$K_N = K_i a + K_m(1 - a) = \frac{1}{At} \cdot \frac{x}{A - x} \text{ when } A = B$$

and $K_N = K_i a + K_m\,(1 - a) = \dfrac{1}{(B - A)t}\, ln\, \dfrac{A(B-x)}{B(A - x)}$

when $A >$ or $< B$

We know the values of A, B and t and can find x by titration. By substituting these values in the equations above we therefore obtain the values for K_N.

By measuring the reaction velocities K_N over a wide range of concentrations we obtain a series of simultaneous equations with different values of K_N, a and $1 - a$, as follows:

$$K_N = K_i a + K_m(1 - a)$$
$$K_N = K_i a' + K_m(1 - a') \text{ etc.}$$

By solving these equations for K_i and K_m we obtain the following values

$$K_i = \frac{K'_N(1 - a) - K_N(1 - a')}{a' - a}$$

and $K_m = \dfrac{K_N a' - K'_N a}{a' - a}$

Johnson and Acree[5] and Robertson and Acree[6] have given a full discussion of the derivation and application of these equations.

[5] Am. Chem. J., 37, 410; 38, 258; 48, 352.
[6] Ibid., 49, 474.

We find that by the use of these equations we obtain constant values for K_i and K_m for any given reaction. Furthermore, if this theory is correct, not only should we obtain constants for K_i and K_m for any given reaction, but K_i should be a constant for the reaction of a given alkyl halide with any ethylate; that is, the ionic velocity should be the same whether the ethylate ions come from sodium, potassium or lithium ethylates. On the other hand K_m may or may not be the same for different reactions. In fact we would expect the molecular velocities to be different in each case. The same, of course, would hold true with the phenolates as with all other analogous substances. That these relations do hold true is shown by the following tables of the values for K_i and K_m for given alkyl halides with different ethylates, phenolates, etc.

Temperature 0°

Reagents	K_i	K_m
Sodium ethylate and methyl iodide	0.004861	0.003033
Sodium ethylate and methyl iodide	0.004960	0.002940
Potassium ethylate and methyl iodide	0.005252	0.003369
Lithium ethylate and methyl iodide	0.005204	0.001974

Temperature 25°

Sodium ethylate and ethyl bromide	0.00576	0.00233
Sodium ethylate and ethyl bromide	0.00543	0.00237
Potassium ethylate and ethyl bromide	0.00539	0.00296
Lithium ethylate and ethyl bromide	0.00574	0.00157
Sodium ethylate and ethyl iodide	0.0120	0.00427
Sodium ethylate and ethyl iodide	0.0122	0.00402
Potassium ethylate and ethyl idiode	0.0122	0.00457
Lithium ethylate and ethyl iodide	0.0122	0.00304
Sodium ethylate and methyl iodide	0.127	0.0594
Sodium ethylate and methyl iodide	0.129	0.0581
Potassium ethylate and methyl iodide	0.126	0.0687
Lithium ethylate and methyl iodide	0.137	0.0387

Sodium phenolate and methyl iodide	0.0282	0.00477
Potassium phenolate and methyl iodide	0.0283	0.00370
Lithium phenolate and methyl iodide	0.0287	0.00393
Sodium phenolate and ethyl iodide	0.00551	0.000987
Potassium phenolate and ethyl iodide	0.00518	0.001011
Lithium phenolate and ethyl iodide	0.00534	0.000910
Sodium thiourazole and ethyl iodide	0.435	0.170
Sodium thiourazole and ethyl iodide	0.463	0.158
Acetimidoethylester catalyzed by sodium ethylate	0.344	0.228
Benzimidoethylester catalyzed by sodium ethylate	0.1172	0.0976
p–brombenzonitrile and sodium ethylate	0.160	0.161
p–brombenzonitrile and potassium ethylate	0.163	0.144
p–brombenzonitrile and lithium ethylate	0.159	0.093

Temperature 35°

	K_i	K_m
Sodium phenolate and methyl iodide	0.0909	0.01310
Potassium phenolate and methyl iodide	0.1036	0.00983
Sodium phenolate and ethyl iodide	0.0183	0.00323
Potassium phenolate and ethyl iodide	0.0197	0.00270
Lithium phenolate and ethyl iodide	0.0174	0.00319

REINTERPRETATION OF THE WORK OF OTHERS

Work of Tubandt

Inversion of methone by sodium ethylate	0.41 at 20°, 0.93	0.41 at 20°. 0.93 at 30°.

Work of J. Stieglitz

Saponification of benzimidonium ethyl ester chloride at 25°	162.0*	50.3*
Saponification of benzimidonium ethyl ester bromide at 25°	163.8*	46.5*
Saponification of benzimidonium ethyl ester nitrate at 25°	163.2*	48.2*

*These values are given in terms of Stieglitz's constants.

Work of Bredig and Stern

Change of benzaldehyde into benzoin by potassium cyanide	0.089	0.089

Work of Hecht, Conrad and Brückner

Sodium ethylate and methyl iodide at 0°	0.005799	0.002649
Sodium ethylate and methyl iodide at 12°	0.02896	0.01028
Sodium ethylate and methyl iodide at 18°	0.06305	0.02003
Sodium ethylate and methyl iodide at 24°	0.12877	0.04354
Sodium ethylate and methyl iodide at 36°	0.5606	0.1892
Sodium ethylate and ethyl iodide at 24°	0.0121	0.00294
Sodium ethylate and ethyl iodide at 36°	0.05282	0.01295
Sodium ethylate and propyl iodide at 36°	0.01025	0.001912
Sodium ethylate and cetyl iodide at 36°	0.01464	0.002541
Sodium ethylate and octyl iodide at 36°	0.01426	0.002407

Work of Bruyn, Lulofs and Steger

	K_t	K_m
Sodium methylate and 1–2–4–dinitrochlorbenzene in absolute methyl alcohol at 15°	1.299	0.724
Sodium methylate and 1–2–4–dinitrochlorbenzene in 90.3 per cent methyl alcohol at 15°	1.376	0.759

Sodium ethylate and 1–2–4–dinitrobrombenzene in absolute ethyl alcohol at 15°	2.838	0.823
Sodium ethylate and 1–2–4–dinitrochlorbenzene in absolute ethyl alcohol at 15°	4.473	1.195
Sodium methylate and o–dinitrobenzene in absolute methyl alcohol at 45°	0.1458	0.1278
Sodium ethylate and o–dinitrobenzene in absolute ethyl alcohol at 45°	0.229	0.230
Work of Segaller		
Sodium phenolate and propyl iodide at 42.5°	0.0128	0.000753
Work of Ostwald		
The inversion of cane sugar		
by hydrochloric acid at 25°	31.2	83.8
by hydrobromic acid at 25°	31.4	93.4
by nitric acid at 25°	31.4	73.1
Work of Koelichen		
The inversion of diacetone alcohol		
by sodium hydroxide	0.2315	0.2315
by barium hydroxide	0.232	0.150

It has been noted that the constants drop off slightly toward the end of the reaction. Several theories have been proposed to explain this phenomenon, among which are a "salt effect," that is the catalytic effect of the salt formed in the reaction or of the ethylate ions or molecules themselves, and (2) the formation of olefines from the alkyl halides.

Arrhenius[7] and later Euler[8] and Stieglitz[9] thought that the "salt effect" was due to the change in activity or ionization of the water by the actions of the salt. Acree[10] has shown that

[7] Z. Phys. Chem., **1**, 110; **4**, 226; **31**, 197.
[8] Ibid., **32**, 348.
[9] Am. Chem. J., **39**, 29, 166, 402, 437, 586, 719; **32**, 221.
[10] Am. Chem. J., 41, 475.

this explanation is untenable because in some cases it would call for a change in the ionization of water many times greater than could probably be caused in this way and also because the same salts in the same concentration sometimes exert a positive and sometimes a negative effect, and hence would have to increase the ionization of water in some cases and decrease it in others, an evident *reductio ad absurdum.* It has also been shown by Acree that in many cases the salt effect is entirely normal, that is corresponding to the change in ionization of the reacting substances by the salt formed. In other cases an "abnormal salt effect" was observed, that is, a "salt effect" which was either too large or too small to correspond to the change in ionization of the reacting substances by the salt formed. Acree also showed that Stieglitz' own work proves that the temperature coefficient of the hydrolysis of imido-ester salts is normal, whereas, on account of the increase in K_m with rise in temperature, the velocities at 18° and 25° would have to be 5 and 9 times, respectively, as large as those observed if the water caused hydrolysis through its ions alone. One side reaction, which may in part explain this decrease in reaction velocity, is the formation of olefines from the alkyl halide. This possibility was pointed out by Shadinger, Marshall, and especially by Robertson.

To check the accuracy of the values for "K_N found" they were compared with the values of "K_N calculated." The latter are found by substituting the proper values of K_i, K_m, α and $1 - \alpha$, for the different concentrations of the ethylates in the equation

$$K_N = K_i\alpha + K_m(1 - \alpha)$$

From these two values, the calculated and found, the per cent error is calculated by using the calculated value of K_N as the standard.

The per cent of reaction due to the ions and to the molecules is found by dividing the values of $K_i\alpha$ and $K_m(1 - \alpha)$, respectively, by the calculated values of K_N for the different concentrations of ethylate.

EXPERIMENTAL

Preparation of Absolute Ethyl Alcohol

The use of the purest alcohol obtainable was necessitated, since it has been shown by several workers[11] in this laboratory and also by Goldschmidt,[12] Lapworth,[13] Bredig and Fraenkel,[14] Kailan,[15] Gyr,[16] and others that reaction velocities are in many cases markedly affected by the presence of small quantities of water. The method which has given best results is to boil up the alcohol with pure lime (400 grams of oxide to the liter) for several days, distil off the alcohol and then repeat the operation, using less oxide the second time. By this method it is easily possible to obtain alcohol containing less than 0.04 per cent of water.

Preparation of Standard Hydrochloric Acid

The hydrochloric acid used in the titrations was made by the method of Hulett and Bonner,[17] by distilling a 20 per cent solution of the acid and thus obtaining a solution of known concentration. This was collected in paraffin bottles which had been thoroughly soaked out and which were kept sealed after the distillation was finished. The acid was made up to the desired strength by weighing out the proper amounts of the constant boiling mixture and of water, and the concentration was checked by silver chloride determinations. The twenty liter bottle in which the acid was kept had been soaked out for several months with dilute acid.

Preparation of the Sodium Ethylate Solution

Sodium ethylate was prepared by dissolving pure sodium in absolute alcohol. As the sodium crust was cut off under kerosene the oil was first roughly removed by wiping the sodium with filter paper. To remove the last traces it was dipped into absolute alcohol before adding it to the alcohol used in making up the ethylate solution. The solution was standardized by

[11] B., **41**, 3227, 3228; Amer. Chem. J., **41**, 457, 483.
[12] B., **39**, 711; Z. Phys. Chem., 60, 728.
[13] J. Chem. Soc., **93**, 2163, 2187; Proc. Chem. Soc., **24**, 101, 152.
[14] Biochem. Z., **6**, 308; Z. Phys. Chem., 60, 202.
[15] B., **39**, 1055; Sitzung Wien, 116, II, 55.
[16] B., **41**, 4322.
[17] J. Amer. Chem. Soc., **31**, 390.

drawing off measured quantities of the ethylate by means of a specially constructed pipette, to be described later, pouring it into water and titrating the sodium hydroxide formed against the standard acid. The flask containing the ethylate was placed in the 0°. bath and alcohol was added to bring the mixture to the proper concentration. The ethylate solution was made up fresh each day, as it turns dark on standing. Shrader has found that this change in color does not materially affect the reaction velocity but that it interferes greatly in determining the end point in titrations.

Preparation of the Alkyl Halide Solution

The alkyl halide solutions were made up by weighing the required amount of the alkyl halide into alcohol in a glass stoppered measuring flask and diluting to the mark with alcohol. Miss B. M. Brown found that 0.3 per cent excess methyl iodide must be added to make up for the loss of the alkyl halide by vaporization.

The Bath

The bath used for this work at 0° was made of copper and lined with tin. It was protected on all sides by pads of lamb's wool and felt. It was kept filled with finely crushed ice and water and was agitated by a specially arranged stirrer. The temperature was found to remain constant to within a few thousandths of a degree.

Machine Pipette

Hecht, Conrad and Bruckner, in carrying out their work on reaction velocities, mixed the solutions of ethylates and alkyl halides in one large flask and withdrew portions at definite time intervals for titration. By this method there is a great possibility for loss of alkyl halide on opening the flask, especially at higher temperatures. Therefore, in the work in this laboratory, small flasks of 20 cc. or 40 cc. capacity were used to contain the individual reaction mixtures.

For transferring the ethylate solution from the large flask in which the solution was made up to the small reaction flasks an ordinary pipette, surrounded by a jacket, which was filled

with crushed ice and water, was used. The jacket was refilled once or twice while the solution was being transferred to the different flasks.

On account of the great volatility of methyl iodide, solutions of this substance cannot be transferred to the reaction flasks by means of the pipette described above, as much would be lost in the operation. To obviate this loss a machine which has been fully described by Robertson [18] was used for measuring out the alkyl halide solution into the small flasks already containing the ethylate. A stream of water from the bath was kept running through the machine in order to keep the temperature of the solution at 0°. Even then a small amount of alkyl halide was lost, but, as mentioned above, this was offset by adding 0.3 per cent excess of methyl iodide when making up the solution. The small flasks were removed from the bath after definite time periods, the contents were poured into about 200 cc. of cold water, and the sodium hydroxide formed from the remaining ethylate was titrated with the standard hydrochloric acid in order to determine the values of x. In these titrations N/5 acid was used with methyl orange as the indicator.

ON THE REACTIONS OF SODIUM ETHYLATE AND METHYL IODIDE AT 0°

Table I—0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
150	2.070	0.001740
180	2.354	0.001709
210	2.647	0.001714
240	2.903	0.001704
	Average	0.001717
	$K_N =$	0.003434

Table II — 0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
150	2.038	0.001706
180	2.323	0.001680
240	2.916	0.001715
264	3.110	0.001708
290	3.314	0.001694
	Average	0.001701
	$K_N =$	0.003402

[18] Amer. Chem. J., **19**, 490.

Table III—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
60	0.515	0.000905
120	0.976	0.000901
210	1.606	0.000911
270	1.980	0.000914
309	2.158	0.000891
397	2.700	0.000901
	Average	0.000904

$K_N = 0.003616$

Table IV—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
60	0.516	0.000906
120	0.976	0.000901
210	1.610	0.000913
270	1.972	0.000909
357	2.460	0.000913
384	2.592	0.000911
	Average	0.000909

$K_N = 0.003636$

Table V—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
118	0.958	0.000898
180	1.418	0.000918
240	1.788	0.000906
1277	5.287	0.000899
	Average	0.000905

$K_N = 0.003620$

Table VI—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
60	0.522	0.000918
120	0.982	0.000908
180	1.379	0.000899
240	1.772	0.000894
300	2.139	0.000903
360	2.448	0.000900
	Average	0.000902

$K_N = 0.003608$

Table VII—0.125 N Sodium Ethylate and 0.125 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
90	0.420	0.000487
150	0.652	0.000465
210	0.912	0.000478
330	1.344	0.000470
390	1.568	0.000476
	Average	0.000475
	$K_N = 0.003800$	

Table VIII—0.125 N Sodium Ethylate and 0.125 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
90	0.426	0.000494
150	0.670	0.000479
270	1.145	0.000479
330	1.352	0.000473
390	1.568	0.000476
	Average	0.000480
	$K_N = 0.003840$	

SUMMARY OF SODIUM ETHYLATE AND METHYL IODIDE AT 0°

Table IX—K_N Found for Sodium Ethylate and Methyl Iodide at 0°

V	K_N	K_N Average
2	0.003434	
	0.003402	0.003418
4	0.003616	
	0.003636	
	0.003620	
	0.003608	0.003620
8	0.003800	
	0.003840	0.003820

Table X--The Ionization of Sodium Ethylate at 0° [19]

V	α	$1 - \alpha$
1	0.136	0.864
2	0.237	0.763
4	0.335	0.665
8	0.435	0.565
16	0.531	0.469
32	0.633	0.367

[19] Robertson and Acree; Diss. J. H. U., 1910; Am. Chem. Jour., 49, 474; Jour. Phys. Chem., **19**, 406.

Table XI—K_i and K_m Found for Sodium Ethylate and Methyl Iodide at 0°

V	K_i	K_m
$V = 2 : V = 4$	0.00499	0.00293
$V = 2 : V = 8$	0.00496	0.00294
$V = 4 : V = 8$	0.00495	0.00295
Average	0.00496	0.00294

Table XII—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 0°

V	K_N Found	K_N Calculated	Error in Per Cent
2	0.003418	0.003419	—0.03
4	0.003620	0.003616	+0.11
8	0.003820	0.003818	+0.05

Table XIII—Per Cent of Reaction Due to Ions and to Molescules

V	Per Cent of Reaction Due to aK_i	Per Cent of Reaction Due to $(1 - a)K_m$
2	34.38	65.62
4	45.95	54.05
8	56.51	43.49

II. Reinterpretation of the Work of Hecht, Conrad and Bruckner on the Reaction of Alkyl Halides With Sodium Ethylate at Different Temperatures.

As was mentioned above, some of the earliest work on the velocities of the reactions of alkyl halides with ethylates was done by Hecht, Conrad and Brückner,[20] but they did not interpret their results according to the ionic theory, as they considered these substances nonelectrolytes (nichtleitende Körper). Since we have shown by actual conductivity measurements that the ethylates are electrolytes, it was interesting to take their data and interpret [21] it on the basis of the reaction of both the ions and nonionized molecules of the sodium and potassium ethylates.

To test this theory we used our conductivity measurements at 0°, 25°, and 35° and calculated the ionization of the ethylate at the temperatures employed by Hecht, Conrad and Brückner. We then substituted these values for a and those found for K_N by Hecht, Conrad and Brückner in the equations:—

$$(1)\ K_i = \frac{K'_N\,(1 - a) - K_N\,(1 - a')}{a' - a}$$

$$\text{and } (2)\ K_m = \frac{K_N a' - K'_N a}{a' - a}$$

and learned that we obtain constants for K_i and K_m which may be considered to check very well with the values found in this laboratory for the same reaction, if we remember the fact that this earlier work had so many sources of error which have since been eradicated.

From their data on the reaction of sodium ethylate and methyl iodide at 0° we obtain $K_i = 0.005799$ and $K_m = 0.002649$, while, for the same reaction, the values found

[20] Z. Phys. Chem., **5**, 289.

[21] Shrader and Acree (Journ. Chem. Soc., **105**, 2582) have made a similar reinterpretation of the work of Segaller.

in this laboratory by Miss Brown are $K_i = 0.004861$ and $K_m = 0.003033$ and the author has found the values $K_i = 0.004960$ and $K_m = 0.002940$. From their data on the reaction of sodium ethylate and methyl iodide at 24° we obtain $K_i = 0.129$ and $K_m = 0.0435$, while for the same reaction at 25° the values found in this laboratory by Miss Brown are $K_i = 0.129$ and $K_m = 0.0581$ and by Robertson $K_i = 0.127$ and $K_m = 0.0594$. From their data on the reaction of sodium ethylate and ethyl iodide at 24° we obtain $K_i = 0.0121$ and $K_m = 0.00294$, while the same reaction at 25°, the values found in this laboratory by Marshall,[22] are $K_i = 0.0120$ and $K_m = 0.00427$, and by Shrader[23] $K_i = 0.0122$ and $K_m = 0.00402$.

It is therefore seen that their work, which was not done from the standpoint of ionic reaction, can be explained very satisfactorily indeed by the theory that both the ions and molecules react side by side.

Hecht, Conrad and Brückner worked out their values for K_N, the reaction velocity, by the use of a purely empirical formula

$$(3) \qquad \begin{aligned} K'_N &= K_N + a \log (V'/V) \\ K''_N &= K_N + a \log (V''/V) \\ K'''_N &= K_N + a \log (V'''/V) \end{aligned}$$

in which K'_N and K_N are the reaction velocities at any dilutions, "a" is an empirical constant, obtained by solving these simultaneous equations, and V'/V is the ratio of the volumes of the two solutions; that is, if we are comparing two solutions, say $V = 10$ and $V = 2$, the V'/V used in the formula above would be the ratio of 10 to 2, which is 5.

As this formula is purely empirical we attempted to find the value of the Hecht, Conrad and Brückner factor "a" in terms of Acree's formula to see if we could find what this term "a" really means; for although their formula is empirical, it seems to hold in practice and it should be possible to give it some rational physical basis.

[22] J. Phys. Chem., 19, 589.
[23] Diss. J. H. U., 1913.

Representing by K'_N and K_N the reaction velocities of two substances at different dilutions we have by Acree's formula :—

(4) $$K_N = K_i a + K_m(1 - a)$$

(5) and $$K'_N = K_i a' + K_m(1 - a').$$

Subtracting we have,

(6) $$K'_N - K_N = K_i(a' - a) - K_m(a' - a)$$
$$= (K_i - K_m)\ (a' - a).$$

According to Hecht, Conrad and Brückner,

$$K'_N = K_N + \text{a log } (V'/V)$$
$$\text{or } K'_N - K_N = \text{a log } (V'/V)$$

Equating these two values for $K'_N - K_N$ we get,

(7) $$\text{a log } V'/V = (K_i - K_m)\ (a' - a)$$

(8) and hence, $$\text{a} = \frac{(K_i - K_m)\ (a' - a)}{\log\ (V'/V)}$$

We then tested this equation (8) to see if we obtain a constant for "a" by substituting the proper values for K_i, K_m, a, a' and V'/V. The tables on pages 26, 27, 28, 31, 34, 37, 41, 44, 46 and 49 show that the values for "a" are really quite constant: since $K_i - K_m$ is also a constant we see that in the work of Hecht, Conrad and Brückner and in the cases studied by us *the difference in ionization of two given solutions seems to be proportional to the logarithm of the ratio of their volumes.* This empirical relation seems to hold over a limited range, especially in the more concentrated solutions, both with those electrolytes which obey the Ostwald dilution law and those which do not. That it cannot hold over all ranges follows at once from the fact that $\frac{(K_i - K_m)\ (a' - a)}{\log\ (V'/V)}$ or "a," becomes gradually smaller and approaches zero for those solutions which are nearly completely ionized. We consider this to be a very important empirical relationship, which we shall develop for all of the cases where the reaction velocities and conductivities are available, whether the substances be organic or inorganic acids, bases and salts.

We then used formula (3) for obtaining the calculated or theoretical values for K'_N, K''_N, K'''_N, etc., by taking any given value as K_N and using the average of the values of *"a"* found above. For uniformity we have called all these values of K'_N, K''_N, K'''_N, etc., simply K_N in the tables. It will be seen from the tables given on pages 26, 27, 28, 31, 35, 38, 42, 45, 47 and 49, that these values for K_N calculated are very close to those found experimentally. From the *"K_N found"* and the *"K_N calculated,"* as explained above, the per cent error was determined, 0.00 error showing the value used as K_N in equation (3). It is clearly recognized that all the values given in the tables below are not accurate beyond the second or third significant figure, even though four are sometimes given.

To test further the relations between the formula used by Hecht, Conrad and Brückner and that used by us, we used some of the work which was done in this laboratory, in which we have eliminated all sources of error as completely as possible, and obtained the values of *"a"* from the equation (8), and of *"K_N calculated"* from equation (3). In our work on sodium ethylate and methyl iodide at 0° the values for *"a"* and for *"K_N calculated,"* obtained from equations (8) and (3), are given in the following tables:—

Table XIV—"a" *Found for Sodium Ethylate and Methyl Iodide at 0°*

	a
$V = 2 : V = 4$	0.000658
$V = 2 : V = 6$	0.000664
$V = 4 : V = 8$	0.000671
Average	0.000664

Table XV—K_N Found, "K_N Calculated," Obtained by Using "a" *in the Equation* $K'_N = K_N +$ "a" *Log* (V'/V) *and Error in Per Cent*

V	K_N Found	K_N Calculated	Error in Per Cent
2	0.003418	0.003418	0.00
4	0.003620	0.003618	+0.06
8	0.003820	0.003818	+0.05

In the work of Shrader on sodium ethylate and ethyl iodide at 25° we find again this close agreement. The average value found for "a" is 0.002297. We given in the following table the values for K_N calculated, the values for K_N found experimentally and the error in per cent.

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.00521	0.00521	0.0
2	0.00595	0.00590	+0.8
4	0.00657	0.00659	—0.3
8	0.00723	0.00728	—0.7
16	0.00800	0.00797	+0.4
32	0.00865	0.00866	—0.1

It is seen that the values for "a" are very constant and that the agreement between the values for K_N found and those calculated is excellent. These are only two of many cases which have been recalculated and in all we find this same excellent agreement.

We therefore find that the empirical formula

$$K'_N = K_N + \text{a log } (V'/V)$$

used so successfully by Hecht, Conrad and Brückner can be transformed into our equations, which have as a rational basis the idea that both the anions and the molecules of the ethylates react with the alkyl halides. This is a beautiful example to illustrate the fact that all valid empirical formulas can be put on a rational basis by the proper study of the questions involved.

ON THE REACTIONS OF SODIUM ETHYLATE AND METHYL IODIDE AT 0°

Table I—K_N Found for Sodium Ethylate and Methyl Iodide at 0°

Conc. $NaOC_2H_5$	K_N Found
1	0.002958
2	0.003426
10	0.003996
20	0.004348

Table II—The Ionization of Sodium Ethylate at 0°

V	a	$1 - a$
1	0.1362	0.8638
2	0.2372	0.7628
10	0.4587	0.5413
20	0.5766	0.4234

Table III—K_i and K_m Found for Sodium Ethylate and Methyl Iodide at 0°

	K_i	K_m
$V = 1 : V = 2$	0.006942	0.002324
$V = 1 : V = 10$	0.005738	0.002518
$V = 1 : V = 20$	0.005616	0.002528
$V = 2 : V = 10$	0.005388	0.003120
$V = 2 : V = 20$	0.005498	0.002780
$V = 10 : V = 20$	0.005612	0.002626
Average	0.005799	0.002649

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 0°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.002958	0.003078	—4.05
2	0.003426	0.003395	+0.91
10	0.003996	0.004099	—2.57
20	0.004348	0.004465	—2.69

Table V—Per Cent of Reaction Due to Ions and to Molecules

V	Per Cent of Reaction Due to aK_i	Per Cent of Reaction Due to $(1 - a)K_m$
1	25.66	74.34
2	40.51	59.49
10	64.89	35.11
20	74.88	25.12

Table VI—a *Found for Sodium Ethylate and Methyl Iodide at 0°*

	"a"
$V = 1 : V = 2$	0.001057
$V = 1 : V = 10$	0.001016
$V = 1 : V = 20$	0.001066
$V = 2 : V = 10$	0.000998
$V = 2 : V = 20$	0.001069
$V = 10 : V = 20$	0.001233
Average	0.001073

Table VII—K_N *Found,* K_N *Calculated by Using* a *in the Equation* $K'_N = K_N + a$ *Log* (V'/V) *and Error in Per Cent*

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.002958	0.002968	0.00
2	0.003426	0.003281	+4.42
10	0.003996	0.004031	—0.86
20	0.004346	0.004354	—0.15

ON THE REACTIONS OF SODIUM ETHYLATE AND METHYL IODIDE AT 12°

Table I—K_N *Found for Sodium Ethylate and Methyl Iodide at 12°*

Conc. $NaOC_2H_5$	K_N Found
2	0.01496
20	0.02014

Table II—The Ionization of Sodium Ethylate at 12°

V	a	$1 - a$
2	0.2360	0.7640
20	0.5275	0.4725

Table III—K_i *and* K_m *Found for Sodium Ethylate and Methyl Iodide at 12°*

	K_i	K_m
$V = 2 : V = 20$	0.02896	0.01028

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 12°

V	K_N Found	K_N Calculated	Error in Per Cent
2	0.01469	0.01468	+0.07
20	0.02014	0.02012	+0.10

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to aK_i	Per Cent of Reaction Due to $(1-a)K_m$
2	46.55	53.45
20	75.92	24.08

Table VI—"a" Found for Sodium Ethylate and Methyl Iodide at 12°

	"a"
$V = 2 : V = 20$	0.005445

Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
2	0.01469	0.01469	0.00
20	0.02014	0.02013	+0.05

ON THE REACTIONS OF SODIUM ETHYLATE AND METHYL IODIDE AT 18°

Table I—K_N Found for Sodium Ethylate and Methyl Iodide at 18°

Conc. $NaOC_2H_5$ V	K_N Found
2	0.03020
10	0.03844
20	0.04642

Table II—The Ionization of Sodium Ethylate at 18°

V	a	$1-a$
2	0.2382	0.7618
10	0.4190	0.5810
20	0.6190	0.3810

Table III—K_i and K_m Found for Sodium Ethylate and Methyl Iodide at 18°

	K_i	K_m
$V = 2 : V = 10$	0.06490	0.01934
$V = 2 : V = 40$	0.06264	0.02004
$V = 10 : V = 40$	0.06162	0.02072
Average	0.06305	0.02003

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 18°

V	K_N Found	K_N Calculated	Error in Per Cent
2	0.03020	0.03026	—0.19
10	0.03844	0.03804	+1.04
40	0.04642	0.04645	—0.06

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to aK_i	Per Cent of Reaction Due to $(1-a)K_m$
2	49.63	50.37
10	69.44	30.56
40	84.04	15.98

Table VI—"a" Found for Sodium Ethylate and Methyl Iodide at 18°

	"a"
$V = 2 : V = 10$	0.01113
$V = 2 : V = 40$	0.01259
$V = 10 : V = 40$	0.01429
Average	0.01267

Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
2	0.03020	0.02993	+0.9
10	0.03844	0.03879	—0.9
40	0.04642	0.04642	0.00

ON THE REACTION OF SODIUM ETHYLATE AND METHYL IODIDE AT 24°

Table I—K_N Found for Sodium Ethylate and Methyl Iodide at 24°

Conc. $NaOC_2H_5$ V	K_N
1	0.05512
2	0.06276
5	0.07182
10	0.07950
20	0.08696
40	0.09448
80	0.10226

Table II—The Ionization of Sodium Ethylate at 24°

V	a	$1 - a$
1	0.1470	0.8530
2	0.2346	0.7654
5	0.3335	0.6665
10	0.4170	0.5830
20	0.5075	0.4925
40	0.6040	0.3960
80	0.7030	0.2970

Table III—K_i and K_m Found for Sodium Ethylate and Methyl Iodide at 24°

	K_i	K_m
$V = 1 : V = 2$	0.1294	0.04230
$V = 1 : V = 5$	0.1215	0.04194
$V = 1 : V = 10$	0.1312	0.04184
$V = 1 : V = 20$	0.1304	0.04212
$V = 1 : V = 40$	0.1284	0.04244
$V = 1 : V = 80$	0.1274	0.04264
$V = 2 : V = 5$	0.1328	0.04126
$V = 2 : V = 10$	0.1330	0.04122
$V = 2 : V = 20$	0.1306	0.04194

	K_i	K_m
$V = 2 : V = 40$	0.1281	0.04260
$V = 2 : V = 80$	0.1273	0.04296
$V = 5 : V = 10$	0.1331	0.04114
$V = 5 : V = 20$	0.1297	0.04280
$V = 5 : V = 40$	0.1276	0.04386
$V = 5 : V = 80$	0.1276	0.04434
$V = 10 : V = 20$	0.1275	0.04510
$V = 10 : V = 40$	0.1262	0.04608
$V = 10 : V = 80$	0.1258	0.04630
$V = 20 : V = 40$	0.1253	0.04740
$V = 20 : V = 80$	0.1255	0.04726
$V = 40 : V = 80$	0.1256	0.04700
Average	0.12877	0.04354

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 24°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.05512	0.05605	—1.68
2	0.06276	0.06352	—1.21
5	0.07182	0.07194	—0.16
10	0.07950	0.07905	+0.57
20	0.08696	0.08676	+0.23
40	0.09448	0.09498	—0.52
80	0.10226	0.10340	—1.17

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to αK_i	Per Cent of Reaction Due to $(1 - \alpha)K_m$
1	33.75	66.25
2	47.53	52.47
5	59.66	40.34
10	67.89	32.11
20	75.28	24.72
40	81.84	18.16
80	87.51	12.49

Table VI—"a" *Found for Sodium Ethylate and Methyl Iodide at 24°*

	"a"		"a"
$V = 1 : V = 2$	0.02478	$V = 5 : V = 10$	0.02362
$V = 1 : V = 5$	0.02272	$V = 5 : V = 20$	0.02461
$V = 1 : V = 10$	0.02299	$V = 5 : V = 40$	0.02551
$V = 1 : V = 20$	0.02359	$V = 5 : V = 80$	0.02613
$V = 1 : V = 40$	0.02429	$V = 10 : V = 20$	0.02560
$V = 1 : V = 80$	0.02488	$V = 10 : V = 40$	0.02645
$V = 2 : V = 5$	0.02116	$V = 10 : V = 80$	0.02697
$V = 2 : V = 10$	0.02222	$V = 20 : V = 40$	0.02730
$V = 2 : V = 20$	0.02324	$V = 20 : V = 80$	0.02765
$V = 2 : V = 40$	0.02416	$V = 40 : V = 80$	0.02801
$V = 2 : V = 80$	0.02489		
		Average	0.02480

Table VII—K_N *Found,* K_N *Calculated by Using* "a" *in the Equation* $K'_N = K_N +$ "a" *Log* (V'/V) *and Error in Per Cent*

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.05512	0.05470	+0.77
2	0.06276	0.06216	+0.96
5	0.07182	0.07202	—0.28
10	0.07950	0.07949	0.00
20	0.08696	0.08696	0.00
40	0.09448	0.09442	+0.44
80	0.10220	0.10189	+0.30

ON THE REACTION OF SODIUM ETHYLATE AND METHYL IODIDE AT 36°

Table I—K_N *Found for Sodium Ethylate and Methyl Iodide at 36°*

Conc. $NaOC_2H_5$ V	K_N Found
1	0.2344
2	0.2664
4	0.2984

V	
5	0.3088
10	0.3408
20	0.3730
40	0.4050
80	0.4370
160	0.4692
1000	0.5540

Table II—The Ionization of Sodium Ethylate at 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3036	0.6964
5	0.3218	0.6782
10	0.3972	0.6028
20	0.4829	0.5171
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134
1000	0.9900	0.0100

Table III—K_i and K_m Found for Sodium Ethylate and Methyl Iodide at 36°

	K_i	K_m
$V = 1 : V = 2$	0.5818	0.1710
$V = 1 : V = 4$	0.5970	0.1656
$V = 1 : V = 5$	0.6100	0.1659
$V = 1 : V = 10$	0.5568	0.1668
$V = 1 : V = 20$	0.5916	0.1693
$V = 1 : V = 40$	0.5730	0.1725
$V = 1 : V = 80$	0.5324	0.1754
$V = 1 : V = 160$	0.5484	0.1771
$V = 1 : V = 1000$	0.5602	0.1754
$V = 2 : V = 4$	0.5968	0.1625
$V = 2 : V = 5$	0.5626	0.1565
$V = 2 : V = 10$	0.6126	0.1616

	K_i	K_m
$V = 2 : V = 20$	0.6068	0.1677
$V = 2 : V = 40$	0.5724	0.1740
$V = 2 : V = 80$	0.5562	0.1787
$V = 2 : V = 160$	0.5620	0.1815
$V = 2 : V = 1000$	0.5576	0.1775
$V = 4 : V = 5$	0.6700	0.1247
$V = 4 : V = 10$	0.6138	0.1609
$V = 4 : V = 20$	0.5572	0.1722
$V = 4 : V = 40$	0.5742	0.1813
$V = 4 : V = 80$	0.5518	0.1878
$V = 4 : V = 160$	0.5446	0.1911
$V = 4 : V = 1000$	0.5574	0.1853
$V = 5 : V = 10$	0.5968	0.1963
$V = 5 : V = 20$	0.5754	0.1806
$V = 5 : V = 40$	0.5614	0.1501
$V = 5 : V = 80$	0.5486	0.1950
$V = 5 : V = 160$	0.5434	0.1978
$V = 5 : V = 1000$	0.5580	0.1907
$V = 10 : V = 20$	0.5666	0.1916
$V = 10 : V = 40$	0.5514	0.2014
$V = 10 : V = 80$	0.5428	0.2076
$V = 10 : V = 160$	0.5392	0.2098
$V = 10 : V = 1000$	0.5576	0.1980
$V = 20 : V = 40$	0.5432	0.2142
$V = 20 : V = 80$	0.5376	0.2196
$V = 20 : V = 160$	0.5302	0.2200
$V = 20 : V = 1000$	0.5574	0.2248
$V = 40 : V = 80$	0.5342	0.2267
$V = 40 : V = 160$	0.5356	0.2247
$V = 40 : V = 1000$	0.5578	0.2491
$V = 80 : V = 160$	0.5362	0.2414
$V = 80 : V = 1000$	0.5586	0.2234
$V = 160 : V = 1000$	0.5584	0.1676
Average	0.5606	0.1892

Table IV—K_N Calculated and Found for Sodium Ethylate and Methyl Iodide at 36°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.2344	0.2464	—4.8
2	0.2664	0.2732	—2.4
4	0.2984	0.3020	—1.1
5	0.3088	0.3087	0.0
10	0.3408	0.3366	+1.2
20	0.3730	0.3686	+1.1
40	0.4050	0.4046	+0.1
80	0.4370	0.4434	—1.4
160	0.4692	0.4814	—2.5
1000	0.5540	0.5568	—0.5

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to αK_i	Per Cent of Reaction Due to $(1-\alpha)K_m$
1	35.11	64.89
2	47.64	52.36
4	56.36	43.64
5	58.42	41.58
10	60.20	39.80
20	73.48	26.51
40	80.41	19.59
80	87.00	13.00
160	91.22	8.78
1000	99.06	0.94

Table VI—"a" Found for Sodium Ethylate and Methyl Iodide at 36°

	"a"		"a"
$V = 1 : V = 2$	0.1064	$V = 5 : V = 10$	0.1001
$V = 1 : V = 4$	0.1070	$V = 5 : V = 20$	0.1054
$V = 1 : V = 5$	0.1066	$V = 5 : V = 40$	0.1176
$V = 1 : V = 10$	0.0948	$V = 5 : V = 80$	0.1068

	"a"		"a"
$V = 1 : V = 20$	0.1064	$V = 5 : V = 160$	0.1068
$V = 1 : V = 40$	0.1065	$V = 5 : V = 1000$	0.1065
$V = 1 : V = 80$	0.0993	$V = 10 : V = 20$	0.1065
$V = 1 : V = 160$	0.1066	$V = 10 : V = 40$	0.1064
$V = 1 : V = 1000$	0.1070	$V = 10 : V = 80$	0.1066
$V = 2 : V = 4$	0.1029	$V = 10 : V = 160$	0.1064
$V = 2 : V = 5$	0.0914	$V = 10 : V = 1000$	0.1064
$V = 2 : V = 10$	0.1064	$V = 20 : V = 40$	0.1063
$V = 2 : V = 20$	0.1102	$V = 20 : V = 80$	0.1062
$V = 2 : V = 40$	0.1064	$V = 20 : V = 160$	0.1042
$V = 2 : V = 80$	0.1065	$V = 20 : V = 1000$	0.0991
$V = 2 : V = 160$	0.1107	$V = 40 : V = 80$	0.1064
$V = 2 : V = 1000$	0.1068	$V = 40 : V = 160$	0.1066
$V = 4 : V = 5$	0.1025	$V = 40 : V = 1000$	0.0905
$V = 4 : V = 10$	0.1064	$V = 80 : V = 160$	0.1003
$V = 4 : V = 20$	0.0986	$V = 80 : V = 1000$	0.0959
$V = 4 : V = 40$	0.1084	$V = 160 : V = 1000$	0.0997
$V = 4 : V = 80$	0.1063		
$V = 4 : V = 160$	0.1064	Average	0.1046
$V = 4 : V = 1000$	0.1064		

Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.2344	0.2357	—0.56
2	0.2664	0.2672	—0.30
4	0.2984	0.2987	—0.11
5	0.3088	0.3088	0.00
10	0.3408	0.3403	+0.14
20	0.3730	0.3718	+0.32
40	0.4050	0.4033	+0.42
80	0.4370	0.4347	+0.52
160	0.4692	0.4662	+0.64
1000	0.5540	0.5495	+0.81

ON THE REACTION OF SODIUM ETHYLATE AND METHYL IODIDE AT 24°

Table I—K_N Found for Sodium Ethylate and Ethyl Iodide at 24°

Conc. $NaOC_2H_5$ V	K_N
1	0.004326
2	0.004946
5	0.006105
10	0.006842
20	0.007624

Table II—The Ionization of Sodium Ethylate at 24°

V	a	$1 - a$
1	0.148	0.852
2	0.235	0.765
5	0.336	0.864
10	0.422	0.578
20	0.512	0.488

Table III—K_i and K_m Found for Sodium Ethylate and Ethyl Iodide at 24°

	K_i	K_m
$V = 1 : V = 2$	0.0104	0.00328
$V = 1 : V = 5$	0.0124	0.00293
$V = 1 : V = 10$	0.0121	0.00297
$V = 1 : V = 20$	0.0120	0.00299
$V = 2 : V = 5$	0.0137	0.00226
$V = 2 : V = 10$	0.0127	0.00258
$V = 2 : V = 20$	0.0123	0.00269
$V = 5 : V = 10$	0.0117	0.00326
$V = 5 : V = 20$	0.0118	0.00323
$V = 10 : V = 20$	0.0118	0.00318
Average	0.0121	0.00294

Table IV—K_N Calculated and Found for Sodium Ethylate and Ethyl Iodide at 24°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.004326	0.004294	+0.7
2	0.004946	0.005090	—2.8
5	0.006105	0.006014	+1.2
10	0.006842	0.006801	+0.6
20	0.007624	0.007625	0.0

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to αK_i	Per Cent of Reaction Due to $(1-\alpha)K_m$
1	41.70	58.30
2	55.86	44.14
5	67.60	32.40
10	75.08	24.92
20	81.25	18.75

Table VI—"a" Found for Sodium Ethylate and Ethyl Iodide at 24°

	"a"
$V = 1 : V = 2$	0.002647
$V = 1 : V = 5$	0.002464
$V = 1 : V = 10$	0.002510
$V = 1 : V = 20$	0.002563
$V = 2 : V = 5$	0.002325
$V = 2 : V = 10$	0.002451
$V = 2 : V = 20$	0.002537
$V = 5 : V = 10$	0.002616
$V = 5 : V = 20$	0.002678
$V = 10 : V = 20$	0.002738
Average	0.002553

Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.004326	0.004302	+0.5
2	0.004946	0.005071	—2.4
5	0.006105	0.006110	0.0
10	0.006842	0.006855	—0.2
20	0.007624	0.007624	0.0

ON THE REACTION OF SODIUM ETHYLATE AND ETHYL IODIDE AT 36°

Table I—K_N Found for Sodium Ethylate and Ethyl Iodide at 36°

Conc. $NaOC_2H_5$	K_N Found
1	0.01817
2	0.02148
4	0.02486
5	0.02586
10	0.02918
20	0.03234
40	0.03594
80	0.03926
160	0.04258
1000	0.05126

Table II—The Ionization of Sodium Ethylate at 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3036	0.6964
5	0.3218	0.6782
10	0.3972	0.6028
20	0.4829	0.5171
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134
1000	0.9900	0.0100

Table III—K_i and K_m Found for Sodium Ethylate and Ethyl Iodide at 36°

	K_i	K_m
$V =$ 1 : $V =$ 2	0.05408	0.01162
$V =$ 1 : $V =$ 4	0.05604	0.01126
$V =$ 1 : $V =$ 5	0.05698	0.01109
$V =$ 1 : $V =$ 10	0.05648	0.01118
$V =$ 1 : $V =$ 20	0.05462	0.01152
$V =$ 1 : $V =$ 40	0.05346	0.01173
$V =$ 1 : $V =$ 80	0.05182	0.01203
$V =$ 1 : $V =$ 160	0.05080	0.01221
$V =$ 1 : $V =$ 1000	0.05164	0.01202
$V =$ 2 : $V =$ 4	0.05782	0.01048
$V =$ 2 : $V =$ 5	0.05900	0.01013
$V =$ 2 : $V =$ 10	0.05730	0.01064
$V =$ 2 : $V =$ 20	0.05474	0.01142
$V =$ 2 : $V =$ 40	0.05338	0.01183
$V =$ 2 : $V =$ 80	0.05168	0.01234
$V =$ 2 : $V =$ 160	0.05070	0.01264
$V =$ 2 : $V =$ 1000	0.05164	0.01235
$V =$ 4 : $V =$ 5	0.06312	0.00818
$V =$ 4 : $V =$ 10	0.05700	0.01084
$V =$ 4 : $V =$ 20	0.05390	0.01219
$V =$ 4 : $V =$ 40	0.05276	0.01273
$V =$ 4 : $V =$ 80	0.05120	0.01337
$V =$ 4 : $V =$ 160	0.05040	0.01372
$V =$ 4 : $V =$ 1000	0.05164	0.01318
$V =$ 5 : $V =$ 10	0.05572	0.01169
$V =$ 5 : $V =$ 20	0.05312	0.01291
$V =$ 5 : $V =$ 40	0.05230	0.01330
$V =$ 5 : $V =$ 80	0.05092	0.01396
$V =$ 5 : $V =$ 160	0.05024	0.01428
$V =$ 5 : $V =$ 1000	0.05162	0.01362
$V =$ 10 : $V =$ 20	0.05140	0.01453
$V =$ 10 : $V =$ 40	0.05144	0.01449
$V =$ 10 : $V =$ 80	0.05034	0.01522

	K_i	K_m
$V = 10 : V = 160$	0.04992	0.01551
$V = 10 : V = 1000$	0.05162	0.01438
$V = 20 : V = 40$	0.05148	0.01445
$V = 20 : V = 80$	0.05010	0.01573
$V = 20 : V = 160$	0.04976	0.01605
$V = 20 : V = 1000$	0.05162	0.01432
$V = 40 : V = 80$	0.04932	0.01744
$V = 40 : V = 160$	0.04956	0.01732
$V = 40 : V = 1000$	0.05162	0.01426
$V = 80 : V = 160$	0.04948	0.01707
$V = 80 : V = 1000$	0.05164	0.01241
$V = 160 : V = 1000$	0.05168	0.00901
Average	0.05282	0.01295

Table IV—K_N Calculated and Found for Sodium Ethylate and Ethyl Iodide at 36°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.01817	0.01910	—5.11
2	0.02148	0.02220	—3.34
4	0.02486	0.02505	—0.76
5	0.02586	0.02577	+0.35
10	0.02918	0.02878	+1.38
20	0.03234	0.03220	+0.13
40	0.03594	0.03607	—0.36
80	0.03926	0.04022	—2.44
160	0.04258	0.04431	—4.06
1000	0.05126	0.05358	—4.52

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to αK_i	Per Cent of Reaction Due to $(1-\alpha)K_m$
1	42.67	57.33
2	55.24	44.76
4	64.01	35.99

V		
5	65.95	34.05
10	72.89	27.11
20	78.59	21.41
40	84.94	15.06
80	89.85	10.15
160	93.76	6.24
1000	97.59	2.41

Table VI—"a" *Found for Sodium Ethylate and Ethyl Iodide at 36°*

	"a"		"a"
$V =$ 1 : $V =$ 2	0.01100	$V =$ 5 : $V =$ 10	0.01101
$V =$ 1 : $V =$ 4	0.01111	$V =$ 5 : $V =$ 20	0.01074
$V =$ 1 : $V =$ 5	0.01101	$V =$ 5 : $V =$ 40	0.01115
$V =$ 1 : $V =$ 10	0.01101	$V =$ 5 : $V =$ 80	0.01116
$V =$ 1 : $V =$ 20	0.01086	$V =$ 5 : $V =$ 160	0.01111
$V =$ 1 : $V =$ 40	0.01110	$V =$ 5 : $V =$ 1000	0.01102
$V =$ 1 : $V =$ 80	0.01106	$V =$ 10 : $V =$ 20	0.01047
$V =$ 1 : $V =$ 160	0.01079	$V =$ 10 : $V =$ 40	0.01123
$V =$ 1 : $V =$ 1000	0.01101	$V =$ 10 : $V =$ 80	0.01117
$V =$ 2 : $V =$ 4	0.01122	$V =$ 10 : $V =$ 160	0.01111
$V =$ 2 : $V =$ 5	0.01100	$V =$ 10 : $V =$ 1000	0.01102
$V =$ 2 : $V =$ 10	0.01101	$V =$ 20 : $V =$ 40	0.01196
$V =$ 2 : $V =$ 20	0.01087	$V =$ 20 : $V =$ 80	0.01148
$V =$ 2 : $V =$ 40	0.01109	$V =$ 20 : $V =$ 160	0.01133
$V =$ 2 : $V =$ 80	0.01109	$V =$ 20 : $V =$ 1000	0.01112
$V =$ 2 : $V =$ 160	0.01108	$V =$ 40 : $V =$ 80	0.01103
$V =$ 2 : $V =$ 1000	0.01104	$V =$ 40 : $V =$ 160	0.01106
$V =$ 4 : $V =$ 5	0.01033	$V =$ 40 : $V =$ 1000	0.01095
$V =$ 4 : $V =$ 10	0.01085	$V =$ 80 : $V =$ 160	0.01102
$V =$ 4 : $V =$ 20	0.01068	$V =$ 80 : $V =$ 1000	0.01122
$V =$ 4 : $V =$ 40	0.01105	$V =$ 160 : $V =$ 1000	0.01088
$V =$ 4 : $V =$ 80	0.01105		
$V =$ 4 : $V =$ 160	0.01104	Average	0.01103
$V =$ 4 : $V =$ 1000	0.01100		

Table VII—K_N Found, K_N Calculated by Using "a" *in the Equation* $K'_N = K_N +$ "a" *Log* (V'/V) *and Error in Per Cent*

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.01817	0.01799	+1.00
2	0.02148	0.02131	+0.79
4	0.02486	0.02463	+0.93
5	0.02586	0.02570	+0.62
10	0.02918	0.02902	+0.55
20	0.03234	0.03234	0.00
40	0.03594	0.03566	+0.78
80	0.03926	0.03898	+0.71
160	0.04258	0.04230	+0.66
1000	0.05126	0.05109	+0.33

ON THE REACTION OF SODIUM ETHYLATE AND PROPYL IODIDE AT 36°

Table I—K_N Found for Sodium Ethylate and Propyl Iodide at 36°

Conc. $NaOC_2H_5$

V	K_N
1	0.002977
2	0.003670*
4	0.004383*
10	0.005312*
40	0.006717
80	0.007420
160	0.008123

* Only experimental values found were:

	K_N
$V = 2$	0.003696
$V = 4$	0.004350
$V = 10$	0.005330

+Values given for K_N above were calculated by the formula of Hecht, Conrad and Brückner.

Table II—The Ionization of Sodium Ethylate at 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3033	0.6967
10	0.3972	0.6028
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134

Table III—K_i and K_m Found for Sodium Ethylate and Propyl Iodide at 36°

	K_i	K_m
$V = 1 : V = 2$	0.01050	0.001604
$V = 1 : V = 4$	0.01096	0.001521
$V = 1 : V = 10$	0.01111	0.001494
$V = 1 : V = 40$	0.01040	0.001621
$V = 1 : V = 80$	0.01007	0.001683
$V = 1 : V = 160$	0.00986	0.001721
$V = 2 : V = 4$	0.01137	0.001341
$V = 2 : V = 10$	0.01131	0.001359
$V = 2 : V = 40$	0.01039	0.001637
$V = 2 : V = 80$	0.01004	0.001743
$V = 2 : V = 160$	0.00984	0.001803
$V = 4 : V = 10$	0.01127	0.001382
$V = 4 : V = 40$	0.01025	0.001826
$V = 4 : V = 80$	0.00994	0.001964
$V = 4 : V = 160$	0.00997	0.002036
$V = 10 : V = 40$	0.00994	0.002261
$V = 10 : V = 80$	0.00974	0.002394
$V = 10 : V = 160$	0.00966	0.002445
$V = 40 : V = 80$	0.00955	0.002799
$V = 40 : V = 160$	0.00957	0.002767
$V = 80 : V = 160$	0.00959	0.002723
Average	0.01025	0.001912

Table IV—K_N Calculated and Found for Sodium Ethylate and Propyl Iodide at 36°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.002977	0.003205	—7.1
2	0.003670	0.003948	—7.1
4	0.004383	0.004455	—1.6
10	0.005312	0.005243	+1.3
40	0.006717	0.006777	—0.9
80	0.007420	0.007650	—3.0
160	0.008123	0.008509	—4.5

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ / V	Per Cent of Reaction Due to aK_i	Per Cent of Reaction Due to $(1-a)K_m$
1	49.59	50.51
2	60.58	39.42
4	70.12	29.88
10	78.03	21.97
40	88.16	11.84
80	92.12	7.88
160	95.22	4.78

Table VI—"a" Found for Sodium Ethylate and Propyl Iodide at 36°

	"a"		"a"
$V = 1 : V = 2$	0.002154	$V = 4 : V = 10$	0.001965
$V = 1 : V = 4$	0.002063	$V = 4 : V = 40$	0.002308
$V = 1 : V = 10$	0.002025	$V = 4 : V = 80$	0.002441
$V = 1 : V = 40$	0.002216	$V = 4 : V = 160$	0.001947
$V = 1 : V = 80$	0.002321	$V = 10 : V = 40$	0.001946
$V = 1 : V = 160$	0.002392	$V = 10 : V = 80$	0.001946
$V = 2 : V = 4$	0.001969	$V = 10 : V = 160$	0.001946
$V = 2 : V = 10$	0.001968	$V = 40 : V = 80$	*0.002883
$V = 2 : V = 40$	0.002229	$V = 40 : V = 160$	*0.002859
$V = 2 : V = 80$	0.002352	$V = 80 : V = 160$	*0.002836
$V = 2 : V = 160$	0.002428		
		Average	0.002247

* Omitting marked values 0.002145

Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.002977	0.003167	—5.9
2	0.003670	0.003823	—4.0
4	0.004383	0.004458	—1.6
10	0.005312	0.005312	0.0
40	0.006717	0.006603	+1.7
80	0.007420	0.007249	+2.3
160	0.008123	0.007894	+2.9

ON THE REACTION OF SODIUM ETHLYTE AND CETYL IODIDE AT 36°

Table I—K_N Found for Sodium Ethylate and Cetyl Iodide at 36°

Conc. $NaOC_2H_5$ V	K_N Found
1	0.004220
4	0.006212
10	0.007530
80	0.010510
1000	0.014140

Table II—The Ionization of Sodium Ethylate at 36°

V	a	$1 - a$
1	0.1543	0.8457
4	0.3036	0.6964
10	0.3972	0.6028
80	0.6842	0.3158
1000	0.9900	0.0100

Table III—K_i and K_m Found for Sodium Ethylate and Cetyl Iodide at 36°

	K_i	K_m
$V = 1 : V = 4$	0.01550	0.002160
$V = 1 : V = 10$	0.01574	0.002116
$V = 1 : V = 80$	0.01427	0.002386
$V = 1 : V = 1000$	0.01426	0.002386

	K_t	K_m
$V = 4 : V = 10$	0.01601	0.001936
$V = 4 : V = 80$	0.01412	0.002776
$V = 4 : V = 1000$	0.01426	0.002770
$V = 10 : V = 80$	0.01380	0.003394
$V = 10 : V = 1000$	0.01425	0.003094
$V = 80 : V = 1000$	0.01426	0.002396
Average	0.01464	0.002541

Table IV—K_N Calculated and Found for Sodium Ethylate and Cetyl Iodide at 36°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.004220	0.004406	—4.40
4	0.006212	0.006213	—0.01
10	0.007530	0.007346	+3.30
80	0.010510	0.010810	—2.85
1000	0.014140	0.014740	—4.24

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to aK_t	Per Cent of Reaction Due to $(1 - a)K_m$
1	51.26	48.74
4	71.53	28.47
10	79.15	20.86
80	92.66	7.34
1000	98.32	1.68

Table VI—"a" Found for Sodium Ethylate and Cetyl Iodide at 36°

	"a"
$V = 1 : V = 4$	0.003308
$V = 1 : V = 10$	0.003309
$V = 1 : V = 80$	0.003303
$V = 1 : V = 1000$	0.003300
$V = 4 : V = 10$	0.003306

	"a"
$V = 4 : V = 80$	0.003311
$V = 4 : V = 1000$	0.003286
$V = 10 : V = 80$	0.003310
$V = 10 : V = 1000$	0.003303
$V = 80 : V = 1000$	0.003392
Average	0.003313

Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
4	0.006212	0.006217	—0.09
10	0.007530	0.007532	—0.03
80	0.010510	0.010524	—0.14
1000	0.014140	0.014154	—0.10

ON THE REACTION OF SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

Table I—K_N Found for Sodium Ethylate and Octyl Iodide at 36°

Conc. $NaOC_2H_5$ V	K_N Found
1	0.003994
4	0.006018
10	0.007294
80	0.010190
1000	0.013700

Table II—The Ionization of Sodium Ethylate at 36°

V	α	$1 - \alpha$
1	0.1543	0.8457
4	0.3036	0.6964
10	0.3972	0.6028
80	0.6842	0.3158
1000	0.9900	0.0100

Table III—K_i and K_m Found for Sodium Ethylate and Octyl Iodide at 36°

	K_i	K_m
$V = 1 : V = 4$	0.01545	0.001902
$V = 1 : V = 10$	0.01548	0.001997
$V = 1 : V = 80$	0.01388	0.002188
$V = 1 : V = 1000$	0.01382	0.002200
$V = 4 : V = 10$	0.01551	0.001879
$V = 4 : V = 80$	0.01365	0.002690
$V = 4 : V = 1000$	0.01381	0.002616
$V = 10 : V = 80$	0.01337	0.003286
$V = 10 : V = 1000$	0.01381	0.002996
$V = 80 : V = 1000$	0.01382	0.002322
Average	0.01426	0.002407

Table IV—K_N Calculated and Found for Sodium Ethylate and Octyl Iodide at 36°

V	K_N Found	K_N Calculated	Error in Per Cent
1	0.003994	0.004235	—6.03
4	0.006018	0.006005	+0.22
10	0.007294	0.007114	+2.49
80	0.010190	0.010510	—3.14
1000	0.013700	0.014140	—3.21

Table V—Per Cent of Reaction Due to Ions and to Molecules

Conc. $NaOC_2H_5$ V	Per Cent of Reaction Due to αK_i	Per Cent of Reaction Due to $(1-\alpha)K_m$
1	51.95	48.05
4	72.09	27.91
10	79.61	20.39
80	92.83	7.17
1000	99.84	0.16

Table VI—"a" Found for Sodium Ethylate and Octyl Iodide at 36°

	"a"
$V = 1 : V = 4$	0.003360
$V = 1 : V = 10$	0.003276
$V = 1 : V = 80$	0.003250
$V = 1 : V = 1000$	0.003230
$V = 4 : V = 10$	0.003203
$V = 4 : V = 80$	0.003200
$V = 4 : V = 1000$	0.003200
$V = 10 : V = 80$	0.003205
$V = 10 : V = 1000$	0.003200
$V = 80 : V = 1000$	0.003289
Average	0.003241

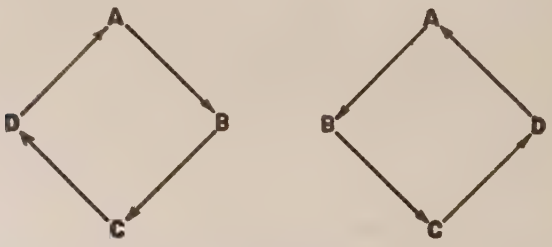
Table VII—K_N Found, K_N Calculated by Using "a" in the Equation $K'_N = K_N +$ "a" Log (V'/V) and Error in Per Cent

V	K_N Found	K_N Calculated	Error in Per Cent
4	0.006018	0.005945	+1.22
10	0.007294	0.007271	+0.39
80	0.010190	0.010212	—0.32
1000	0.013700	0.013757	—0.42

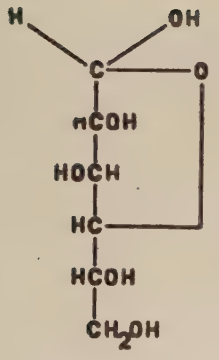
III. On the Configurations of α and β Glucose

Glucose has the empirical formula $C_6H_{12}O_6$. Five of these oxygen atoms are in the form of hydroxyl groups but the sixth is in a combination which shows some of the properties of aldehydes. For instance, the presence of the hydroxyl groups is shown by the fact that it forms compounds resembling alcoholates when treated with metallic hydroxides and forms esters when treated with organic acids, acid anhydrides and acid chlorides. It was thought for a long time that the aldehyde structure is the proper one, but the great stability toward many reagents does not indicate the presence of a free aldehyde group.

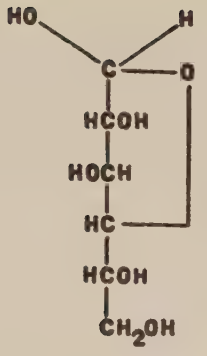
The first light on these apparent discrepancies in the constitution of glucose was given by Tollens when he suggested the lactone formula, in which we have a ring consisting of four carbon atoms and one oxygen atom. According to Tollens' idea these four different carbon atoms can be arranged in two ways, represented thus—



so that we may have two stereo-isomers. We now represent these two forms of glucose, which we designate as the α and β forms, in the following way:—



α methyl glucoside



β methyl glucoside

In taking up our work on the sugars our problem was to determine which of these configurations represents the α and which the β form, as it was not possible to decide this with certainty from the work done up to that time.

Armstrong thinks that one of the differences lies in the fact that the hydroxyl groups are at different distances from the oxygen of the lactone ring. He draws this conclusion from the difference in the rates of hydrolysis of the α and β methyl glucosides, the glucosides having configurations similar to the α and β glucose. His view [24] is as follows:—

"Considering the hydrolysis of the glucosides two views are possible, either (1) that the compound behaves much as the simple ether $CH_3 \cdot O \cdot CH_3$ would, and that the hydrolyst becomes associated with the oxygen atom to which the CH_3 group is attached; or (2) that the attachment is to the oxygen atom in the ring. On the former view the two isomeric α and β glucosides should be hydrolysed with equal readiness as the methoxyl groups are equally weighted in the α and β positions.

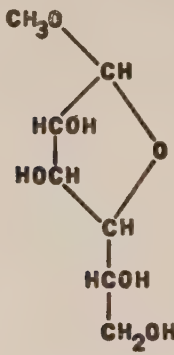
"Actually in the case of both glucose and galactose the β derivative is hydrolysed about 1.75 times as readily as the α derivative, and, as there is every reason for thinking that the

[24] Monographs on Biochemistry,—The Simple Carbohydrates and the Glucosides, page 86.

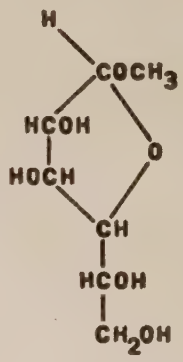
mechanism of change is the same in both cases, the difference in the rate of hydrolysis can only be due in main to the relative distances of the OCH_3 groups from the center of change.

"There is little doubt that the active system within which change takes place, is formed by the association of acid-water molecules with the oxygen atom in the pentaphane ring. Oxonium compounds are formed of the type already discussed at length on pp. 19, 22. In other words, this oxygen is the centre from which attack proceeds.

"Reference to a solid model will readily show that a distinct difference exists in the relative distances of the OCH_3 group, when in the α and β positions, from the oxygen atom in the ring; this is but imperfectly rendered on a plane surface.



α methyl glucoside



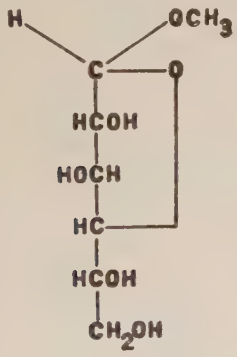
β methyl glucoside

"The α methyl glucoside since it is the most stable form, may be assumed to be that in which the methoxyl (OCH_3) group is furthest removed from the pentaphane oxygen as shown above; conversely, the β glucoside will be that in which the methoxyl is nearest the oxygen centre."

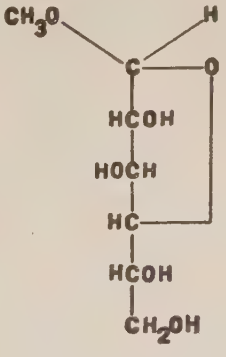
It will readily be seen that this view does not explain the configuration, for if the four carbons and the oxygen atom of the five-membered ring lie in the same plane, as we have every reason to believe, the H–C–OCH_3 group must lie in a plane perpendicular to the plane of the lactone ring and the OCH_3

will be at the same distance from the oxygen of the lactone ring, no matter on which side of this ring it is found. Armstrong believed that in the β glucoside the OCH_3 group is adjacent to the hydroxyl of the α carbon.

From his work on the dissociation constants of the methyl glucosides, Michaelis[20] comes to different conclusions as to the configuration. For α methyl glucoside he finds the value $K = 1.97 \times 10^{-14}$ and for β methyl glucoside $K = 2.64 \times 10^{-14}$. It is known that a positive grouping will diminish the acidic properties of the neighboring hydroxyl group and that this effect becomes greater and greater the nearer the positive group lies to the hydroxyl group. He therefore concludes that in the α compound the positive OCH_3 group must be on the same side of the molecule as the hydroxyl group of the α carbon, and in the β compound it is on the opposite side of the molecule as shown in the following formulas:—



α methyl glucoside



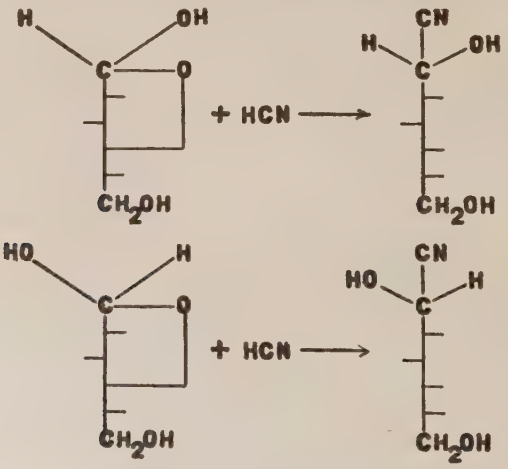
β methyl glucoside

From ordinary glucose and 3 per cent prussic acid Fischer obtained 35 per cent of the theoretical amount of α glucoheptonic acid. He states that the yield was poor because of the great solubility of the lactone of the acid in water. He obtained some of the β compound from the residue after the α acid was cystallized out but does not state the yield, so that we can draw no conclusions as to the structure of the original

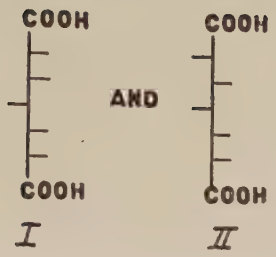
compound from which he started. Any conclusion drawn from the present evidence must favor the idea that the α compound is the one on the left above.

Since much of the above evidence is physical it was deemed wise to attempt to solve this question by applying some chemical reactions which would enable us to determine the configurations of the α and β glucose from the configurations of the products obtained. Accordingly our method of attacking the problem was to try to effect the addition of absolute hydrocyanic acid to the α and β glucose, or some substitution product of these compounds, to form the cyanhydrine and then to change the cyanhydrine into the dibasic acid. Absolute hydrocyanic acid was used because the sugars show mutarotation in water solution with acids and alkalies and it was thought that this could be prevented entirely, or reduced to a minimum by using the absolute acid.

If the HCN were to add to the two different forms of glucose we would expect it to do so in the following manner:—



When these cyanhydrines are hydrolyzed and the CH_2OH groups oxidized to COOH we should obtain the two heptonic acids:—



We could readily distinguish between these two acids, as I would be optically inactive, while II would be optically active, and from the relative yields in the two cases we could tell the configurations of the α and β compounds with which we started.

EXPERIMENTAL

Preparation of Pure α Glucose [25]

Eight hundred grams of ordinary commercial glucose was heated with 80 cc. of water in a large flask on a steam bath until all of the sugar was dissolved. The flask was then removed from the bath and 800 cc. of glacial acetic acid, which had been previously warmed to 70°, was added. This was thoroughly mixed and filtered with suction while hot. The filtrate was of a dark red color but brilliantly clear. This acetic acid solution was seeded and allowed to crystallize for 24 hours, after which time it was filtered and washed with glacial acetic acid until the filtrate was colorless. The yield was 507 grams. This is principally, if not wholly, anhydrous α glucose.

This crystallized α glucose was purified as follows:—It was melted in a flask on the water bath with 75 cc. of water. When completely melted it was cooled to the room temperature and 95 per cent alcohol added with continuous shaking until a white opalescence began to appear, due to the precipitation of of the syrupy phase. This required about 200 cc. of alcohol. This solution was warmed on the water bath until clear and filtered hot. The filtrate was allowed to run into an evaporat-

[25] This method was devised by Dr. C. S. Hudson, to whom we are indebted for much valuable advice.

ing dish containing 100 cc. of 95 per cent alcohol. Crystallization began at once and about 200 cc. of 95 per cent alcohol was added and the mass stirred to keep it thin. The solution was allowed to crystallize over night, 100 cc. 95 per cent alcohol was added to thin the mass again and the sugar filtered off with suction. It was then washed with 95 per cent alcohol until the filtrate was colorless. About 1 litre of alcohol was necessary. The crystallized α glucose was dried in the air. The yield was 340 grams.

Preparation of α Methyl Glucoside

Thirty-eight grams of pure α glucose was placed in a flask, 380 grams of absolute methyl alcohol added and dry hydrochloric acid passed in till the solution was saturated. The glucose slowly went into solution as the hydrochloric acid was absorbed. The solution was allowed to stand until it no longer reduced Fehling's solution. About three-fourths of the alcohol was then distilled off and a part of the methyl glucoside precipitated out. No more precipitated on standing but we found that it could be driven out of solution by adding dry acetone. The yield was poor but was greatly increased by the use of acetone. The methyl glucoside was recrystallized from ethyl alcohol and was found to be comparatively pure as it melted at 164°. The melting point given by Fischer is 165°–166°.

Preparation of α Pentacetyl Glucose

Two hundred grams of acetic anhydride was placed in a flask with a little fused sodium acetate and 40 grams of pure α glucose added. On warming, the glucose melted and formed a layer on the bottom of the flask. A vigorous reaction then took place, the temperature rising to 140°. When the reaction was completed the solution was poured into a large volume of water. The pentacetyl glucose separates out first as a thick syrup, but by frequently changing the water it comes out as a white crystalline solid. For purification it was twice dissolved in acetic acid and reprecipitated by water. The

yield was 30 grams. The melting point was 130°, Fischer obtaining 134°.

Preparation of Absolute Hydrocyanic Acid

A mixture of 10 parts of potassium ferrocyanide, 7 parts of concentrated sulphuric acid and 14 parts of water was placed in a 10 liter retort on a sand bath and heated to drive over the hydrocyanic acid. Two condensers were used. Water, which had been heated to 30°, was forced through the first one to condense any water vapor and cause it to flow back into the retort while the acid could pass on. The second condenser was a double jacketed one for liquefying the hydrocyanic acid. The water passing through this one was first cooled in a long lead coil immersed in an ice bath. The liquid hydrocyanic acid was collected in a suction flask immersed in a freezing mixture. To prevent the escape of the acid vapors a U tube was connected to the side tube of the flask and then imbedded in the freezing mixture. It was found that practically none of the vapors escaped from the flask. To remove all traces of moisture a large quantity of phosphorus pentoxide was added and the acid redistilled from it. The yield was 81 per cent of the theoretical.

Experiments with Hydrocyanic Acid and Glucose and Its Derivatives

About 5 cc. of absolute HCN was added to 1 gram each of α glucose, β glucose and fructose in separate test tubes and the tubes allowed to stand in ice for three weeks. At the end of this time none of the sugars had gone into solution. They were filtered off and tested for nitrogen by several methods. First the solid substance was heated with metallic sodium in a test tube to convert any of the CN group into NaCN. The tube while hot was then dropped into a few cc. of water and the glass and carbon filtered off. Then a few drops of a solution of a ferrous and a ferric salt were added, the solution heated and then made acid to dissolve any hydroxide of iron

which was formed. If the CN group were present we should get a green or blue color. The test was negative in each case. The substance was also heated with an alkali to see if any ammonia was given off. These tests were also negative.

In another experiment 30 grams of β glucose were placed in a 250 cc. bottle and 150 cc. of absolute HCN and six drops of water added. The stopper was wired down and the bottle allowed to stand for two months at the ordinary temperature. The HCN was then filtered off. The filtrate was evaporated to dryness but no residue was left, this fact showing that the glucose was not dissolved. The solid was dried and tested as above but gave no test for nitrogen. The solution remained perfectly clear throughout the two months.

To another tube containing 1 gram of α glucose and 5 cc. of the absolute acid a few drops of water were added and the tube kept in ice. After about two weeks all of the glucose had gone into solution. The HCN was distilled off as completely as possible and the residue placed in a vacuum desiccator. A thick syrup was left but no test for nitrogen was obtained.

Five cc. of 80 per cent HCN was placed in a test tube and as much α glucose added as would dissolve. The solution was allowed to stand at 0° for two weeks. There was a distinct layer on the bottom of the tube but no cyanhydrine was obtained.

Two and five-tenths grams of α pentacetyl glucose were placed in a bottle with 75 cc. of absolute HCN and the solution allowed to stand for 3 days. The acid was then distilled off and a crystalline solid was left. The product was evidently the unchanged pentacetyl glucose as it gave no test for nitrogen.

Five grams of α pentacetyl glucose was dissolved in 15 cc. of glacial acetic acid and the solution allowed to stand for two weeks. The HCN and acetic acid were then distilled off and a white solid remained which gave no test for nitrogen.

Five grams of α pentacetyl glucose was treated with 50 cc. of absolute HCN and water added until the pentacetyl glucose just began to precipitate. First a clear layer was formed

on top of the solution but this disappeared on shaking. The solution was allowed to stand at the ordinary temperature for about two days and the HCN and water distilled off under diminished pressure. A slightly brown substance crystallized out, the color presumably being due to the polymerization of the HCN. A sample was dissolved in ether, the brown substance filtered off and the ether solution evaporated until a white precipitate was given. This substance gave a melting point of 130° and by tests appeared to be the unchanged pentacetyl glucose.

Five grams of α pentacetyl glucose was dissolved in 100 cc. of dry benzene and about 15 cc. of absolute HCN added. The solution was allowed to stand for two weeks. The acid and benzene were distilled off under diminished pressure. A white residue was left which, according to tests, was the unchanged pentacetyl glucose.

IV. The Equilibrium Between Mucic Acid and Its Lactones

Preparation of Pure Mucic Acid

In a large evaporating dish 400 grams of milk sugar and 4,800 grams of nitric acid (specific gravity 1.15) were placed and the solution evaporated with stirring to about 800 cc. In this way we obtained a syrupy mass due to the separation of the mucic acid. After cooling, the mass was diluted with water, filtered and washed with cold water. For purification the acid was dissolved in dilute alkali and precipitated with hydrochloric acid.

In the preparation it was found that unless very dilute alkali were used the sodium salt formed was dissolved with great difficulty. The best results were gotten by using 3–4 per cent alkali and dissolving the acid in the cold. In this way a purer product was obtained, with very little loss of acid, as it is practically insoluble in water.

In attempting to determine the solubility of mucic acid in water we found that some lactone was formed in the water solution and that the amount of lactone was greatly increased if the solution were boiled. We also saw that after some time equilibrium was established between the acid and lactone.

A quantitative study of this equilibrium was then taken up. In this work we made up three different solutions of mucic acid at different temperatures. In all three instances we had an excess of acid present. The first was made up at room temperature, the second was kept at 30° for one hour, and the third at 100° for 30 minutes. All three were placed in a constant temperature bath at 25° and shaken from time to time. Measured quantities were withdrawn from each for titration after definite time periods. A piece of filter paper was tied over the end of the pipette to keep the solid particles

of acid from being drawn up. It was found that if the solution were poured into ice water the mucic acid could be titrated with standard alkali without affecting the lactone. To determine the amount of lactone present in the solution an excess of standard alkali was added, the solution boiled for a few minutes, and the excess alkali titrated with N/10 hydrochloric acid. Phenolphthalein was used as the indicator.

In the following table is given *t*, the time in hours, the amount of N/10 alkali necessary to neutralize the free acid and the amount necessary to neutralize the lactone. The amount of the solutions withdrawn for titration was, in each case, 25 cc.

Solution Made Up at Room Temperature

t	Cc. Alkali Necessary to Neutralize Acid	Cc. Alkali Necessary to Neutralize Lactone
2	1.63	0.25
4.5	1.70	0.68
28.5	1.65	0.81
52	1.60	1.00
100	1.62	1.16
172	1.64	1.46
258	1.55	1.85
720	1.55	2.13
1440	1.65	3.39

Solution Kept at 30° for 1 Hour

t	Cc. Alkali Necessary to Neutralize Acid	Cc. Alkali Necessary to Neutralize Lactone
3	1.90	0.80
26	1.82	0.78
50	1.70	0.90
74	1.68	1.20
146	1.67	1.42
242	1.65	1.69
1440	1.65	3.21

Solution Kept at 100° for 30 Minutes

t	Cc. Alkali Necessary to Neutralize Acid	Cc. Alkali Necessary to Neutralize Lactone
3	20.93	19.07
5	19.63	18.95
27	11.12	19.50
51	8.46	17.02
99	7.12	17.62
171	6.00	16.75
267	5.40	14.55
1440	3.76	9.99
2880	1.66	3.42

From this data it is seen that equilibrium is reached in the first two solutions in 1,440 hours, while for the third it required 2,880 hours. At equilibrium it required 1.65 cc. of alkali to neutralize the free acid and 3.34 cc. to neutralize the lactone, so that there is almost exactly twice as much of the lactone as acid in the solution. Whether this lactone is the mono or di-lactone, or both, we cannot tell from the data but we shall study some of the monobasic acids to follow the rate of formation of the lactone where we can have only the mono lactone formed. It will also be seen from the tables that the amount of acid in the first two solutions remains nearly constant throughout, while the amount of lactone steadily increases. In the third solution both the acid and lactone gradually decrease in amount.

BIOGRAPHY

William A. Taylor, the author of this dissertation, was born in Jarrettsville, Maryland, November 6, 1886. He received his early education in the public schools of that town, and in 1903 was graduated from the Jarrettsville High School. He then attended Randolph-Macon Academy, Front Royal, Virginia, for one year, and in the fall of 1904 entered Randolph-Macon College. He was graduated in 1908, receiving the degrees of Bachelor of Arts and Master of Arts. The two succeeding years were spent in teaching in the High Schools of Sulphur Springs, Texas, and Belair, Maryland. After spending one year in a business office in Belair, Maryland, he entered Johns Hopkins University in the fall of 1911 as a graduate student in Chemistry, with Physical Chemistry and Applied Electricity as his subordinate subjects. During the year 1912–13 he was lecture assistant in organic chemistry.